Sources and fate of nitrogen oxides

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Sources and fate of nitrogen oxides

*almost* Everything has been said.

*Keep* your attention.
Tropospheric NO$_2$: The global picture

- For the first time ever!
- Meanwhile: >10 years, 4 satellite instruments
- Spatial resolution much better than global CTM/GCMs
Tropospheric NO$_2$: What can we learn?

- Check our understanding on emissions and chemistry of nitrogen oxides:
  - Where are the sources?
  - What is the strength of the different NO$_x$ sources?
  - Trends
  - Transport and deposition of NO$_x$ → Chemistry!
Tropospheric NO$_2$: **Restrictions**

- Stratospheric estimation
- Sensitivity, AMF
  - Albedo
  - Profile
  - Clouds & Aerosols
- Fixed local time
- Limited spatial resolution
Tropospheric NO$_2$: **How to use?**

- Comparisons/combinations with (inverse) models
  - Loss of spatial and temporal resolution
  - Resulting product: Model or measurement?

→ Gain as much info as possible from the meas.
Tropospheric NO$_2$: What will I talk about

- Present some studies on
  - Source identification & quantification
  - Estimating lifetimes
- This is a workshop:
  - Some questions
Sources of NO\textsubscript{x}

Mean tropospheric slant column density (TSCD) (SCIAMACHY 2003-now)

- Fossil fuel comb. 22 (13-31)
- Biomass burning 8 (3-15)
- Lightning 5 (2-20)
- Soil emissions 7 (4-12)

Tg [N]/year

(Lee et al. 1997)
Fossil fuel combustion

• >50%
• „Stationary“ sources (transport on prescribed tracks)
  → Constant spatial patterns
  – Cities
  – Power plants
  – Highways?
  – Ship tracks

• Characteristic temporal patterns:
  – Seasonal variations
  – Holidays, temporal regulations → Wang et al., 2007
  – Weekly cycle!
Fossil fuel combustion: **Ship emissions**

- High uncertainties: 3-7 Tg [N]/yr
- Up to 1/3 of total NO\textsubscript{x} emissions from combustion!
- Strong impact: low background NO\textsubscript{x}
- Probably strong increase during next decades
Fossil fuel combustion:

**Ship emissions**

a) Estimated NO\textsubscript{x} emissions based on **AMVER** (Endresen et al., 2003)

b) NO\textsubscript{2} TVCD GOME (Spring, Cloud free)

c) Meridional **high-pass** filtered TVCD

*Beirle et al., 2004*

→ *Richter et al., 2004*
Fossil fuel combustion: **Ship emissions**

**AMVER ship traffic density**

2003-2004 mean, Land masses masked

**SCIAMACHY NO₂**
Fossil fuel combustion: **Ship emissions**

- **AMVER ship traffic density**
  - 2003-2006 mean, 2D Highpass-filtered
  - Land masses masked

- **SCIAMACHY NO$_2$**
  - 2003-2006 mean, 2D Highpass-filtered
  - Land masses masked
Fossil fuel combustion: **Ship emissions**

- **Future:**
  - Better statistics, increasing ship emissions
    → more & clearer ship tracks
  - Interaction of ship emissions and sensitivity due to aerosols and clouds???
  - Check: 1+1=2?
  - Gaps???

2003-2006 mean, 2D Highpass-filtered
*Land masses masked*
Fossil fuel combustion: **Weekly cycle**

**US Eastcoast**

**Europe**

Tropospheric NO$_2$ mean vertical column density (GOME, 1996-2001)

*Beirle et al., 2003*
Fossil fuel combustion: **Weekly cycle**

Normalized weekly cycles of NO₂ for different parts of the world.
Fossil fuel combustion: **Trends**

- China: strong increase

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*Richter et al., 2005*

→ *Van der A et al., 2006*
Fossil fuel combustion: **Trends**

- Narrow Swath: use GOME high resolution to reconstruct past spatial distribution!

→ **Beirle et al., Highly resolved global distribution of tropospheric NO\textsubscript{2} using GOME narrow swath mode data, Atmos. Chem. Phys., 4, 2004.**
Biomass burning

- Characteristics:
  - Seasonality
  - Indicator: Fire counts

  \[ \rightarrow \text{Thomas et al., 1998} \]
  \[ \rightarrow \text{Spichtinger et al., 2004} \]

- Problems:
  - Saturation
  - Aerosols!
  - Profiles!
  - Lifetime!
  - Different emission factors

\[ \rightarrow \text{Very difficult to get quantitative!} \]
Soil emissions

• Triggered by rain
  → Strong temporal fluctuations

→ Jaegle et al., 2004
→ Ron
Lightning

• Importance:
  – UT: low background, long lifetime
  → Strong impact on UT ozone
  – High uncertainties!

• Characteristics:
  – Seasonality
  – Max. over tropical land masses

• Specific problems:
  – Profile?
  – UT: low NO₂/NOₓ
  – Clouds
Lightning

- Correlation of lightning and NO$_2$

**Correlation** of monthly mean **flashes** (LIS) and NO$_2$ (GOME) for Australia $\Rightarrow$ 2.8 (0.8-14) Tg[N]/yr

Lightning

Boersma et al., 2005:
Correlation of GOME NO$_2$ and TM3 LNO$_2$:
1.1-6.4 Tg [N]/yr
Martin et al., 2007:
Comparison of
SCIAMACHY
NO$_2$
GEOS-Chem:
4-8 Tg [N]/yr
Lightning

Unresolved issues:
Lightning parameterizations don’t match Congo maximum!

Global Lightning Apr 1995-Feb 2003 LIS / OTD (NASA)

Central Africa:
• **Highest flash rate** globally
• **15%** of global flashes
→ **15%** of global LNO$_x$ production
• Upper bound: Don’t care (too much) about biomass burning...

• Rough estimate of $LNO_x$:
  - cloud free: $<1.7$ Tg N/yr (same assumptions as for Australia case study)

• Extrapolation not critical: 15% of global flashes!
• **Upper bound**: Don‘t care (too much) about biomass burning...

• **Rough estimate** of LNO$_x$:
  cloud free, same assumptions as for Australia case study

<1.7 Tg [N]/yr
Lightning: **Direct observation** of fresh LNO₅

Case study on August 30 2000 in the Gulf of Mexico
Lightning: **Direct observation** of fresh LNO$_x$

\[
V^{NO_x} = f \cdot S^{NO2}
\]

- Conversion factor depends on box AMF and NO$_2$ profile, i.e. LNO$_x$ profile and NO$_x$ partitioning:

\[
f = \frac{1}{\sum p_i^{NOx} \cdot l_i \cdot a_i}
\]

- $a_i$: Box Air Mass Factor (AMF)
- $p_i$: normalized NOx profile
- $l_i$: NO$_x$ partitioning $L = [NO_2]/[NO_x]$
\[ f = \frac{1}{\sum p_i^{NOx} \cdot l_i \cdot a_i} \]

\[ \Rightarrow V^{NOx} = f \cdot S^{NO2} \]

**LNO\textsubscript{x} profile:**
Cloud resolving models
*Pickering et al. 1998*
*Fehr et al. 2004*

**NO\textsubscript{x} partitioning:**
In-situ measurements in New Mexico for cb conditions
*Ridley et al. 1994, 1996*

**Box AMFs:**
(sensitivity)
RTM, cb conditions
*Hild et al. 2002*

\[ \ldots = 4.02 \ (2.12-7.14) \]
Lightning: **Direct observation of fresh LNO\textsubscript{x}**

- 4 years of **SCIAMACHY** data
- 3 years of **WWLLN** data (global continuous ground based lightning counts)
- Automated search for „lightning events“ prior SCIAMACHY overpass:
  - grid WWLLN flash counts 5-10 local time on 1°x1° grid
  - mask pixels with >20 flashes („lightning pixel“)
  - identify clusters of connected lightning pixels with more than 200 flashes in total
  - keeping lightning clusters that are (partly) covered by SCIAMACHY
  - **1680 matches!!!**
Lightning

SCIAMACHY NO$_2$ for WWLLN lightning events 2004-2006

- local time 10 a.m. → almost all over ocean
- high fluctuations (logarithmic scale)
- low NO$_2$ signal
Lightning: Direct observation of fresh LNO$_x$

• What is different???
Lightning: Direct observation of fresh LNO$_x$

- **What is different???

Flashes on 2004/10/07 at 23:05 and 24h before

Flashes on 2005/03/05 at 23:21 and 24h before
Lightning

• What is the reason for the high variability in NO₂?
  – **No dependency** of NO₂ on
    • Flash counts
    • CTH
    • Flash time
  – **Regional differences!?**

• Where is the LNOₓ?
  – Gulf of Mexico case study: LNOₓ production at lower end!
  – observed NO₂ enhancement 1.6*10^{15} molec/cm²
  – expected: 2.5*10^{16} molec/cm²
    (250 mol per flash, conversion as in the Gulf of Mexico case study)
Lightning

Estimates of $\text{LNO}_x$ from UV/vis sats

• 2.8 (0.8-14) Beirle et al., 2004
• 1.9 (0.5-9.5) Beirle et al., 2004 with updated global flash rate
• 1.1-6.4 Boersma et al., 2005
• 1.7 (0.6-4.7) Beirle et al., 2006
• 4-8 Martin et al., 2007
• <1.7 Congo cloud free
• ??? Direct SCIAMACHY obs.

→ What’s wrong?
Transport …

- BL: short lifetime of NO$_x$, moderate wind speeds
  - Annual mean NO$_2$ distribution reflects emissions
- Events of medium/longrange transports also happen
  - Wenig et al.,
  - Stohl et al.,
  - Talk by Mijling
... and **lifetime**

- Transport is determined by wind and lifetime
  - empirical analysis of transport holds information on lifetime
- Lifetime:
  - Hard to measure
  - Models: nonlinearity, coarse spatial resolution!
  - Necessary to estimate emissions from NO$_2$ columns
Lifetime: Simple estimates

Leue et al., 2001:
Mean lifetime ~ 24 hours

- Problems:
  - Multiple, extended sources
  - GOME pixel width (decrease in SCIAMACHY much steeper)
    → lifetime overestimated!
  - Mean($\text{NO}_2$ * wind) $\neq$ mean($\text{NO}_2$) * mean(wind)
Lifetime: Simple estimates

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Fit: $\tau = 4.2 \text{ h}$ – at 70°N!
Lifetime: Simple estimates

- **Ship tracks:** *(Beirle et al., 2004)*
  - Winds relatively stable
  - North-South: good GOME resolution
  - Remaining uncertainty due to daily variation of tau

**Lifetime estimation:**
- **2.3 hours** (summer)
- **5.1 hours** (winter)
Lifetime: Advanced estimates

- Model transport: FLEXPART
- Consider a point source: Riad
- Model spatial patterns for different lifetimes
Lifetime: Advanced estimates

Normalized sections of constant longitude (46° E) crossing Riad
Using wind data

General additive model:
Dependency of NO₂ TSCD on Wind direction

\[ y = \mu + s_1(\theta_{wind}) + s_2(\text{day in year}) + \text{slope} \cdot t + s_3(\text{day in week}) \]

GOME-data 1996-2000, ECMWF wind data

M. Hayn, satellite Group Mainz-Heidelberg
Using wind data

- NO$_2$-plumes can be followed across the ocean
- determination of “influence zone”

GOME-data 1996-2000, ECMWF wind data

M. Hayn, satellite Group Mainz-Heidelberg
Using wind data: „Fluxes“

- „Flux“ of NO$_2$: Mean(NO$_2$ * wind)
- Quantify transport
- Ocean fertilization
- Lifetime

GOME-data 1996-2000,
ECMWF wind data

M. Hayn, satellite Group Mainz-Heidelberg

Preliminary
Using wind data: „Fluxes“

GOME-data 1996-2000, ECMWF wind data

M. Hayn, satellite Group Mainz-Heidelberg
Normalized seasonal weekly cycles of NO$_2$ for Germany

# Lifetime: Weekly cycle again...

<table>
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<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
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</table>

**Measured lifetime**, independent on models

Fossil fuel combustion: **Weekly cycle**

- **Fri / (Sun-Thu)**
- **Sat / (Mon-Fri)**
- **Sun / (Mon-Fri)**
- **Mon / (Tue-Fri)**
What comes next?

- Dealing with the open questions:
  - Clouds
  - Lightning NO\textsubscript{x}

- Ongoing measurements, GOME-2
- Different overpass times
- More and more use of spatial and temporal subsets (even on daily scale)
- Source identification: more+improved „trigger“
- More+improved external datasets
- Chemistry: combination with other trace gases: HCHO, CHOCHO, trop. O\textsubscript{3} etc.